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TRANSIENTS IN RAPID REACTIONS BY COMBINED MOLECULAR BEAM-MASS S--ETC(U)

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termed molecular beam analysis, combines mass spectrometry of ions with molecular beam characterization of neutrals prior to ionization, in order to achieve unambiguous identification of intermediates in gaseous reactions. In favorable cases, a sensitivity of 10^{11} cm^{-3} has been attained. Using a steady-state flow-tube reactor, molecular beam analysis has been employed for kinetics studies of the reactions of F with CCl_4 , CF_3I , CCl_3Br and CF_3Br ; of Cl with HCl and of Br with F_2 . Additionally, chemiluminescence generated in reactions of atomic fluorine was surveyed, and that in the combination reaction of H with F studied in detail. A gas phase titration for fluorine atoms was developed and used in a measurement of the rate constant for homogeneous recombination of fluorine atoms. Weak rf discharges were evaluated as sources of reactive intermediates for kinetic studies.

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Understanding and control of reacting gaseous systems requires knowledge of the particular elementary reactions occurring in the system and of the rate constants of these elementary reactions. Although such information can occasionally be obtained from experiments in which only bulk properties (eg, T or P) or concentrations of stable reactants or products are measured, the use of methods which directly monitor the transient intermediates participating in the elementary reactions greatly increases the confidence and accuracy of the analysis. Powerful spectroscopic techniques, which are sensitive to extremely low concentrations of particular intermediates, have been developed during the last decade. Mass spectrometry, however, remains a useful general tool for this purpose. The work under the present contract has dealt mainly with the development of new systematic experimental procedures, whereby a number of molecular beam techniques are employed to enhance the usefulness of mass spectrometry in monitoring transient intermediates in gaseous reactions. We have termed this synthesis molecular beam analysis^{1,2,13}.

Briefly, molecular beam analysis combines the ability of mass spectrometry to measure mass-to-charge ratios of ions with the ability of molecular beam measurements to determine properties of the neutral parents of these ions. For example, deflection of the molecular beam by an inhomogeneous magnetic field indicates which ions arise from paramagnetic neutrals (free atoms and radicals) and which are generated from diamagnetic molecules. Likewise, an inhomogeneous electric field can identify polar parents of an ion. Finally, measurements of neutral velocities by a time-of-flight method permits an estimation of the mass of

the neutral parent of an ion, in the limit of effusive flow sampling from a reactor. Recently we have shown that an interesting synergism can be obtained by combining the time-of-flight and magnetic deflection dimensions of our apparatus. With this combination we have been able to monitor separately the $^2P_{3/2}$ and the $^2P_{1/2}$ states of atomic fluorine in reactive systems¹³. Unfortunately, relaxation of $^2P_{1/2}$ is so rapid, that these experiments were unable to resolve separate rate constants for these two states of the fluorine atom.

In molecular beam analysis, the parent neutral of each ion is identified by molecular beam measurements and no use is made of selective ionization by controlled-energy electrons. Thus, the ionizer of the mass spectrometer can be operated under conditions which maximize ionization efficiency. Several stages of differential pumping between the reactor and the ionizer minimize background pressure modulation and filament poisoning which adversely affect many other mass spectrometers employed for kinetics studies.

The apparatus for molecular beam analysis has evolved through the course of our ONR contract. Initially, a small permanent hexapolar magnet was employed for deflection of paramagnetic particles. Recently this has been replaced by a focusing electromagnet, with insulated pole tips, which allows electric deflection to be studied without a time-consuming change of the deflecting field¹³. A new sampling configuration has allowed more efficient collection of intermediates that are rapidly destroyed on surfaces¹³, and increased pumping speed has permitted operation with more intense molecular beams. Recently, our apparatus has been interfaced to a laboratory computer for more efficient data handling.

Initially, because of ONR interest in advanced oxidizers for propulsion, we applied molecular beam analysis to studies in gaseous fluorine kinetics. At this time there was very little literature in this field. Our study of the $F + CCl_4$ reaction was the first absolute measurement of an atomic fluorine reaction incorporating direct measurement of fluorine atom concentration⁴. While measuring the rate constant of the $F + CCl_3Br$ reaction, we demonstrated the importance of rapid atom-switching reactions, such as $F + CCl_3 \rightarrow Cl + CCl_2F$ ⁵. Fluorine atoms were found to react with CCl_4 , CCl_3Br , and CF_3I by an abstraction rather than a displacement mechanism^{4,5}. A similar reaction, $F + CF_3Br$, where the abstraction channel is endothermic, was found to result in addition of the fluorine atom, to form a stable "psuedotrihalogen" radical⁶. Subsequently, Y. T. Lee and coworkers have found similar species to be important in a number of crossed molecular beam reactions.

Building on the expertise we had developed in generating, handling and measuring the concentration of atomic fluorine, we surveyed the chemiluminescence produced when various gases were reacted with fluorine atoms⁷. In the case of hydrocarbons, CH and C_2 bands were observed, similar to what is produced in oxygen-supported combustion of hydrocarbons. In the case of Cl_2 , atomic chlorine recombination emission ($A \rightarrow X$ of Cl_2) was observed. The concentration dependence of the intensity of this emission suggested that Cl_2 could serve as a titrant for atomic fluorine in the presence of F_2 , with the endpoint indicated by the relative intensity of the chemiluminescence⁷. This titration has been used by a number of investigators in studies of fluorine kinetics. The Cl_2 titration was used by us to measure the rate constant for

homogeneous recombination of fluorine atoms⁹. Surprisingly, this reaction is a hundred-fold slower than the recombination reactions of Cl, Br, I, N, O, and H.

The utility of the Cl₂ titration depends upon the very slow rate of the Cl + F₂ reaction. The Br + F₂ reaction was also found to be very slow, and the temperature dependence of its rate constant was investigated¹⁰. Br₂ also appears to be a suitable titrant for atomic fluorine in the presence of F₂. The N + F₂ reaction was investigated and found not to proceed at a conveniently measureable rate at room temperature.

Weak visible chemiluminescence observed in the F/F₂/H₂ system was studied in detail and found to be due to HF vibrational overtone bands ($\Delta v = 5$ and 6) produced by atom combination¹². We have been attempting to develop a visible laser from this reaction and plan to continue this work with funding provided by Emory University. The principal investigator has combined with Professor Ruby Foon of the University of New South Wales, Australia, to review the "Kinetics of Gaseous Fluorine Reactions" for Progress in Reaction Kinetics¹¹.

Recently, our kinetics studies have concentrated on atomic chlorine reactions. A study of atomic chlorine recombination in the presence of HCl has suggested the importance of a stable ClHCl intermediate as a route for the enhanced recombination rate observed in this system¹⁴. In addition, on a grant from the Manufacturing Chemists Association, we have been using molecular beam analysis to study the Cl + SO₂ + M → ClSO₂ + M and Cl + OCS reactions, both of potential importance in connection with the destruction of stratospheric ozone by chlorine resulting from anthropogenic emissions of chlorofluoromethanes.

In an attempt to develop a general method for producing reactive intermediates for kinetics studies, molecular beam analysis was employed to analyze the products formed when a variety of complex molecules were passed through weak rf discharges. Although many interesting species were produced by this route and some understanding of processes occurring in discharges achieved, few of these systems were "clean" enough (containing a single predominant reactive species) to be used for kinetics work¹³. Some of our discharge studies involved analyzing for stable end products by gas chromatography. To aid in such measurements, a novel method of increasing the sensitivity of gas chromatographic analysis of low pressure systems was developed. In this method, a low pressure sample is trapped in a Teflon bag and compressed to atmospheric pressure prior to injection into the gas chromatograph⁸.

Some studies of ionization in fluorine-supported combustion, using total ion collection methods, were performed. Ionization was noted with a variety of hydrocarbons. With H_2 as a fuel, ionization was greatly reduced. We hope to continue this work with funding from Emory University. ONR will be notified of any further progress in this area.

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